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NOVEL TRANSETHERIFICATION IN CATALYTIC REDUCTION OF 4-ALKOXYNITROBENZENES IN ALCOHOL-SULFURIC ACID SOLUTION[1)]

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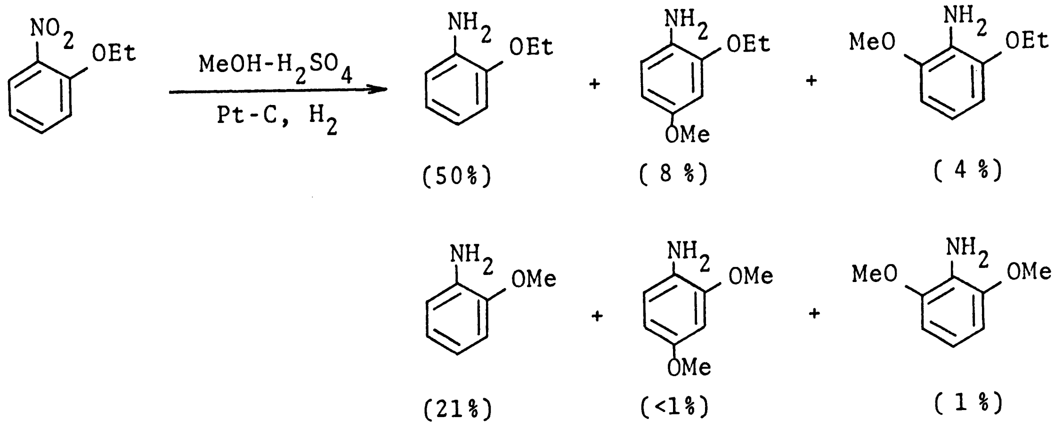
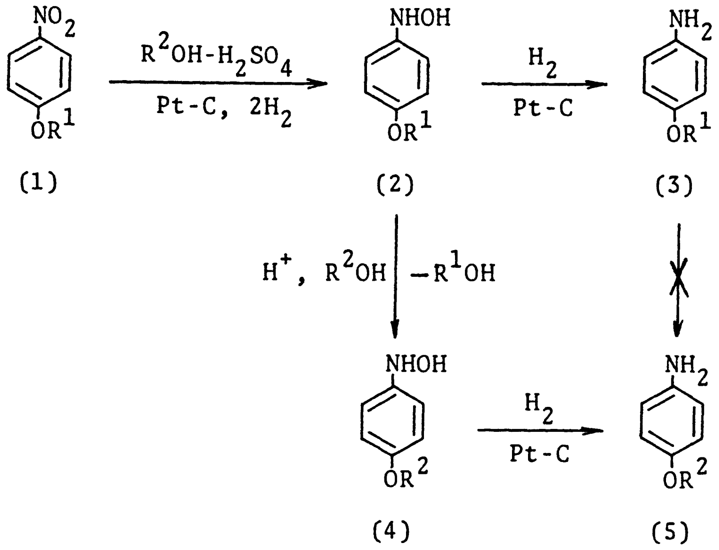
In catalytic reduction (5% Pt-C, 1 atm H_2) of 4-alkoxynitrobenzenes (R^1O-C_6H_4-NO_2) in alcohol(R^2OH)-sulfuric acid solution at room temperature, the reduction was found to be accompanied by transetherification to afford R^2O-C_6H_4-NH_2.

We reported previously that catalytic reduction of 2-substituted nitrobenzenes in methanol-sulfuric acid solution gave 4-methoxyanilines as well as reduced anilines.[2)] We proposed that 4-methoxyanilines are formed via a Bamberger-type rearrangement of the intermediate phenylhydroxylamines. As an extension of the study, we carried out catalytic reduction of 2-nitrophenetole in methanol-sulfuric acid solution and unexpectedly found that the reaction system yields, in addition to conventional reduction and rearrangement products, 2-anisidine and 2,4- and 2,6-dimethoxyaniline. The result indicates that transetherification has occurred in this reaction medium (Scheme 1).[3)]



Scheme 1

Futher, to investigate the novel transetherification reaction in a more simplified system,[4)] we employed 4-alkoxynitrobenzenes(1) as substrates (Scheme 2).



Scheme 2

Catalytic reduction of 4-nitroanisole(1, R^1=Me) in ethanol (R^2=Et)-sulfuric acid gave 4-anisidine(3, R^1=Me), 4-phenetidine(5, R^2=Et), and 4-aminophenol(6, R^2=H in 5). The yields are recorded in Table 1. Among the reaction conditions tested (see footnote to Table 1), the transetherification product (5) became maximum(35%) at H_2SO_4 2.0-3.0 g. Further increase in the amount of sulfuric acid enhanced the yield of 6 (up to 45%) but not that of 5. On the other hand, the yield of 5 was enhanced up to 45% when dimethyl sulfoxide was added to deactivate the catalyst at H_2SO_4 1.0 g.

Table I Catalytic reduction of 4-nitroanisole with hydrogen in ethanol-sulfuric acid[a)]

H_2SO_4 (g)	Yield/% [b)] (3, R^1 = Me)	(5, R^2 = Et)	(6)[c)]
1.0	52	28	14
2.0	43	35	18
3.0	38	35	19
5.0	24	30	45
1.0[d)]	34	45	10
2.0[d)]	19	41	35
3.0[d)]	20	36	42

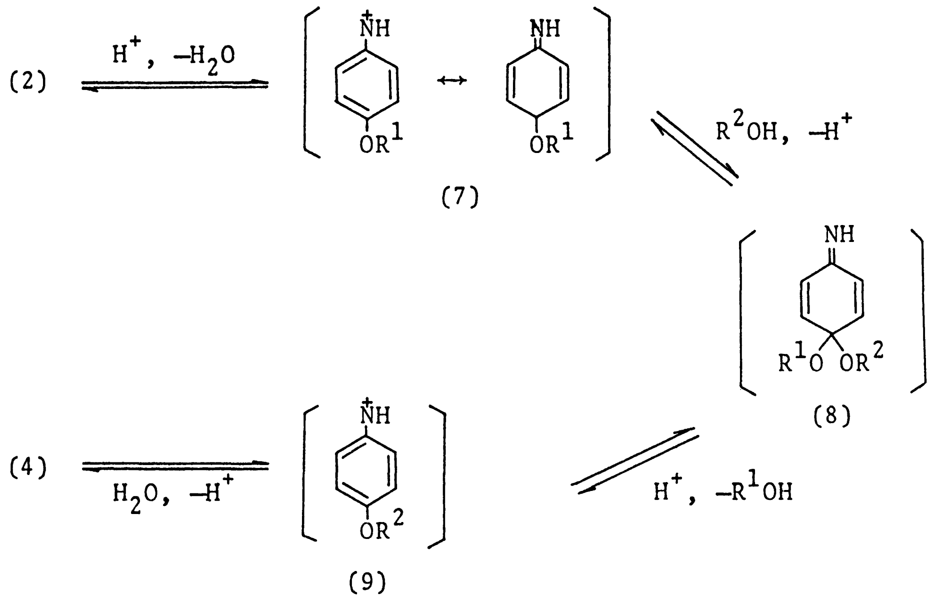
a) Reaction conditions: 4-nitroanisole = 1.99 g, EtOH = 20 ml, 5% Pt-C = 60 mg, 1 atm of H_2, room temperature; reaction time = 3-6 hrs, 5-12 hrs[d)].

b) Yields were determined by GLC and diazo-titration method.

c) (6) = (5; R^2 = H)

d) DMSO (50 µl) was added to deactivate the catalyst.

The reaction routes to 5 and 6 would be shown as follows (Scheme 3): (i) like a mechanism of Bamberger rearrangement,5) nitrenium ion (↔ carbonium ion, 7) from 2 undergoes nucleophilic attack of alcohol(R^2OH) or water(produced by the reaction of alcohol and sulfuric acid) to give ketal(or hemiketal, 8), (ii) alcohol(R^1OH) is eliminated from 8 to give another nitrenium ion (9), (iii) hydroxylamine (4) bearing the R^2O group is produced, which finally affords 5, like the reaction 2 → 3. The reaction scheme is quite symmetric with respect to R^1O and R^2O.



Scheme 3

The mechanism in Scheme 3 is supported by several experimental results: (i) the increase in sulfuric acid leads to the increase in the yields of 5 and 62) (in particular, for 6),5) (ii) catalytic reduction of 2-nitrophenetole in methanol-sulfuric acid solution gives 2,4- and 2,6-dimethoxyaniline which are the Bamberger-type rearrangement products from 2-methoxyphenylhydroxylamine4), a transetherification product, and (iii) the yields of 5 and 6 are enhanced by dimethyl sulfoxide which poisons the catalyst.2) We further corroborated that neither 5(R^2 = Et or Me) nor 6 is afforded from 3(R^1 = Me or Et) under the present reaction conditions.

Finally, we examined the possibility of the transetherification reaction in several systems (Table 2). Clearly, transetherification products are obtained in relatively good yields, indicating the versatility of the transetherification in alcohol-sulfuric acid solution.

Table 2 Catalytic reduction of 4-alkoxynitrobenzenes(1) with hydrogen in alcohol-sulfuric acid solution[a)]

<table>
<tr><th>(1)</th><th>R^2OH</th><th colspan="3">Yield/%</th></tr>
<tr><th>R^1=</th><th>R^2=</th><th>(3)</th><th>(5)</th><th>(6)</th></tr>
<tr><td>Me</td><td>Et</td><td>43</td><td>35</td><td>18</td></tr>
<tr><td>Me</td><td>n-Pr</td><td>47</td><td>20</td><td>17</td></tr>
<tr><td>Me</td><td>n-Bu</td><td>46</td><td>12</td><td>23</td></tr>
<tr><td>Me</td><td>i-Pr</td><td>44</td><td>10</td><td>10</td></tr>
<tr><td>Et</td><td>Me</td><td>46</td><td>39</td><td>11</td></tr>
<tr><td>Me</td><td>Me</td><td colspan="2">75</td><td>9</td></tr>
</table>

a) Reaction conditions: (1) = 13 mmol, R^2OH = 20 ml, H_2SO_4 = 2.0 g, 5% Pt-C = 3 wt% of (1), 1 atm of H_2, room temperature; reaction time = 3-6 hrs.

REFERENCES

1) Studies on Bamberger-type Rearrangement. VI.

2) T. Sone, S. Katada, Y. Okiyoshi, S. Shinkai, and O. Manabe, Nippon Kagaku Kaishi, in press.

3) The yields in parentheses were those at H_2SO_4 2.5 g (other reaction conditions, see footnote to Table 1).

4) Catalytic reduction of 2-alkoxynitrobenzenes in alcohol-sulfuric acid gave both 4- and 6-substituted rearrangement products, whereas 2-substituted rearrangement products were not detected from 4-alkoxynitrobenzenes (e.g., T. Sone, M. Karikura, S. Shinkai, and O. Manabe, Nippon Kagaku Kaishi, 1979, 1532).

5) T. Sone, Y. Tokuda, T. Sakai, S. Shinkai, and O. Manabe, J. Chem. Soc., Perkin Trans. II, 1981, 298.

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